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ADSORPTION, MOBILITY AND ORGANIZATION OF ORGANIC MOLECULES AT CLAY SURFACES PROBED BY PHOTOPHYSICS AND PHOTOCHEMISTRY

FOURTH INTERIM REPORT

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Contents

1. Introduction

2. Experimental results

A. Photopolymerization of methacryloxyethylmethyldidodecyl ammonium chloride (DDMEMEC) on a Laponite surface in aqueous media.

B. Discontinuity at low loadings of 3-(1-pyrenyl) propyltrimethylammonium chloride in absence and presence of various detergents

C. Time dependence at low loadings of clay suspensions

D. Synthesis of pyrene labeled silica sterically stabilized silica particles.

a. synthesis and purification

b. characterization and spectroscopy

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Introduction

In the previous report, the study of the adsorption of a polymerisable detergent, namely methacryloyloxyethyl methyldidodecyl ammonium chloride, on a clay surface has been initiated. The monomeric adsorption is further investigated and some polymerization have been performed.

The aggregation phenomena of adsorbed detergentlike molecules have been further investigated in detail, by studying clay suspensions with varying loadings of probe and detergents. Especially at low loadings some interesting observations have been made.

In the previous report a time dependence of the clay suspensions has been mentioned. This phenomena is also further investigated. In addition to spectroscopic techniques, viscosity and light scatter measurements have been used to study this time dependence.

In addition to clay suspensions, a study of silica suspensions is initiated. In order to avoid exchange phenomena of the adsorbed molecules between the particles an attempt has been made to attach the probes to the silica particle by means of a covalent bond. This enables a more quantitive study of particle interactions.

For the adsorption on a clay surface, 3-(1 pyrenyl)propyltrimethylammonium bromide (PN) has again been used as fluorescent probe. The work presented in this report was performed on Laponite, a synthetic Hectorite

PHOTOPOLYMERIZATION OF METHACRYLOYL OXYETHYL METHYL DIDODECYL - AMMONIUM CHLORIDE (DDMEMEC) ON LAPONITE SURFACE IN AQUEOUS MEDIUM.

DDMEMEC, adsorbed on a clay surface, has been polymerized by irradiating at 366 nm, using AIBN as initiator. I.R. and Raman spectroscopy were used to see wether polymerization took place or not. The advantage of Raman spectroscopy is that the aqueous suspension, could be measured immediately after irradiation. In figure 1 the raman spectra before and after irradiation are shown. Before irradiation a bond at 1660 cm^{-1}, which can be ascribed to the double bond of the monomer, is observed. This bond disappears after irradiation. This indicates that a polymerization took place. For the I.R. measurements, an attempt has been made to separate the polymer from the clay surface. This was done by adding 1N HCl to the clay suspension, followed bye an extraction with chloroform. HCl is added to remove the polymer from the surface. Once the polymer is detached, it will go to the organic phase, due to its insolubility in water. The I.R. spectra of the monomer and the polymer are shown in figure 2. The monomer shows two peaks in the 1800 - 1600 cm^{-1} region which can be ascribed to the double bond (1630 cm^{-1}) and the carbonyl group(1725 cm^{-1}).

The polymer only shows a peak at 1725 cm^{-1} .The double bond has disappeared which again indicates polymerization of the monomer. Beside the photochemical polymerization, a thermal one was also performed with $K_2S_2O_8$ as initiator. Again Raman spectroscopy indicates that a polymerization took place. Some of the polymerizations were performed in the presence of 3-(1-pyrenyl)trimethylammonium chloride as photophysical probe. In all cases, an increase of the excimer formation is observed after polymerization. The same result is obtained when the probe is added after polymerization. This could indicate a segregation of the adsorbed molecules during polymerization. Work is in progress to characterize the polymer and to study the influence of the polymer on the rheology of the clay suspensions.

B. DISCONTINUITY AT LOW LOADINGS OF 3-(1-PYRENYL)PROPYL TRIMETHYLAMMONIUM BROMIDE IN ABSENCE OR PRESENCE OF VARIOUS DETERGENTS.

In the previous report, the spectroscopic properties of adsorbed PN, at various loadings, on Laponite was reported. An interesting result was the observed discontinuity in absorption and emission properties at a loading of 15%. of the Cation Exchange Capacity (C.E.C.). In order to gain additional information about this phenomenon, more experiments have been performed. In all these experiments the loading of the adsorbed molecules was kept between 0 and 20 % of the C.E.C.

The observation that at a loading of 15 % of PN, a steep increase of the ratio of the excimer and the monomer emission (I_e/I_m) is observed, suggests a modification of the distribution and/or orientation of the adsorbed molecules on the clay surface. In this experiment, the loading was varied by keeping the probe concentration constant and changing the clay concentration. An analogue experiment, I_e/I_m as a function of the loading of PN, was performed, but now by keeping the clay concentration constant and by varying the probe concentration. Again, a discontinuity is observed, but now at 10 % of the C.E.C.

The difference between these two values can be due to the non-homogeneous distribution of the adsorbed molecules on the clay surface. This suggests that the C.E.C. is not a very good parameter to indicate the concentration on the clay surface. Indeed the C.E.C. reflects the local concentration only when the distribution of adsorbed molecules is homogeneous.

The same experiment has been performed on Hectorite and Barasym. The results are shown in figure 3 .With Barasym, analogue results are obtained as for Laponite. With Hectorite however no discontinuity is observed. I_e/I_m increases monotonously with PN concentration. It is clear that the adsorption of PN on Laponite and Barasym has the same characteristics. It is known that adsorption on Laponite and Barasym occur only at the external surface, at least at relatively low loadings. On Hectorite however, the molecules adsorb both on the external and the interlamellar surface. In fact, for Hectorite, the ratio external to total surface is small.

In a previous report was already shown that a distinction can be made between excimers formed on the external surface and those formed at the interlamellar surface. Indeed, excimers formed at the interlamellar surface have an fluorescence maximum at 375 nm while those formed at the external surface have a maximum at 480 nm.

Another difference between Hectorite on one hand and Laponite and Barasym on the other, are the excitation spectra. With Laponite and Barasym, these become very distorted after the discontinuity, while for Hectorite the excitation spectra remain the same as a function of the loading.

In figure 4 the ratio I_e/I_m is given as a function of detergent concentration. The detergents used are CTAC and DDAC and the clay was Laponite. The dependence of I_e/I_m is the same for both detergents: a decrease with a discontinuity at a loading of detergent of about 5 % of the C.E.C. The values of I_e/I_m with DDAC are however lower than those with CTAC, because DDAC shield the PN molecules more efficient from each other as described in a previous report. This discontinuity has also been observed for the polymerisable detergent.

It seems that the discontinuity in the spectroscopic behaviour only appears for molecules adsorbed on the external surface of the clay particles. It is also known that molecules on the interlamellar surface, contrary to those adsorbed on the external surface, are very well shielded from the surrounding medium, which in our case is water.

A possible explanation would be that the aqueous surrounding induces, at a certain concentration, a reorganisation of the adsorbed molecules. From literature (1-3) it is known that detergents or detergentlike molecules adsorbed on a surface form so called hemimicelles at a certain concentration: the critical hemimicellar concentration. Very little however is known about the structure of such a hemimicelle. Some authors suggest that before the critical hemimicellar concentration the detergents are adsorbed as individual molecules and form a micellarlike structure at the critical hemimicellar concentration. Others however suggest that already before the critical hemimicellar concentration an aggregation between the detergent molecules occurs. At the critical concentration however, this aggregation becomes more pronounced. In this case the hemi-

micelles are comparable with fragmented double-layers. Such double-layers are frequently called admicelles (4) Indeed, for detergents it is energetically more favourable to form double layers. In such a double layer the polar head groups are situated at the surface and in the water phase and the apolar chains are very well shielded from the water. A recently published theoretic study on the structure of aggregates of adsorbed surfactants on mineral oxide surfaces indicates that a high surface charge density and a high dielectric constant favour the formation of admicelles before the formation of a hemi-micelle. This study is based on the calculation of the chemical potential of the monomer in a hemimicelle or an admicelle.

To our knowledge, no information is available about hemi-micelle or double-layer formation of detergents on a clay surface in suspension, at low loadings. It is however known that at full saturation of the clay surface, detergents can form a double layer.

Based on the theory, presented in a former paragraph, the formation of an admicelle on the surface of Laponite and Barasym would not be very surprisingly. Indeed, these clays have a rather high surface charge density and the dielectric constant is the one of water, which is high.

If the discontinuity in our experiments indicates a reorganisation of the adsorbed molecules on the clay surface, the presence of ground state interactions and a very efficient excimer formation indicate that already before the reorganisation, interactions between the adsorbed molecules exist. If the reorganisation is a formation of an admicelle, the increase in excimer formation indicates that there is a considerable interpenetration of the second layer in the first one.

Due to the assumption of micellarlike aggregates on the clay surface, a function used in micellar media has been used to fit the fluorescence decay of PN, adsorbed on a clay surface in the presence of detergent molecules. Such a function has also been used by Van Damme et al. (5,6) to fit the fluorescence decay of pyrene adsorbed on a silica surface, covered with detergent molecules. They used a kinetic scheme where the exchange of the probe between "micelles" is negligible. These authors found that in a certain concentration range

the fluorescence decay of the monomer and the excimer can be described by assuming a Poisson distribution of the pyrene in micellarlike aggregates.

In an ideal system, no excimer fluorescence is observed at sufficiently low concentrations of PN. In this situation none or only one pyrene molecule is solubilized in a "micelle" and consequentially no excimer formation is observed. In our case however it seems impossible to obtain such an ideal system. One reason is certainly the limited amount of detergent which can be adsorbed on the clay surface, due to a flocculation at higher detergent concentrations. This phenomenon limits the ratio detergent/probe to about 200. It is possible that at this ratio the probability of more than one PN residing in the same "micelle" is not zero, resulting in an excimer formation.

When the fluorescence decay of the monomer is fitted to micellar kinetics, without exchange between the "micelles", good statistical parameters are obtained. From the obtained parameters the aggregation number of the "micelles" can be calculated. These values are however always too low and are dependent on the PN concentration. A possible explanation is that the probe does not explore the entire "micelle" during its life time. Therefore the obtained aggregation numbers are too small. The portion of the "micelle" which is explored by the probe becomes smaller when the concentration increases. This results in a decrease of the aggregation number as a function of the concentration as observed.

Another explanation is of course that micellar kinetics are not applicable in our system. More work is in progress to elucidate the fluorescence decay of PN adsorbed on a clay surface.

C. TIME-DEPENDENCE AT LOW LOADINGS OF CLAY SUSPENSIONS.

In figure 3 the ratio I_e/I_m for P3N adsorbed on Laponite (1g/l) is given as a function of time. An increase of this ratio is observed, until it remains constant after several days. This increase is less pronounced when the sample was degassed every day. In figure

5 the viscosity of a Laponite suspension (1g/1) is shown, again as a function of time, both with and without probe adsorbed at the surface. The viscosity of both samples decreases with time until a constant value is obtained, again after several days. The viscosity of the Laponite suspension however, containing P3N, decreases more rapidly. It seems that there is a nice correlation between the I_e/I_m ratio and the viscosity as shown in figure ...

These observations certainly indicate that even a very diluted Laponite suspension undergoes initially some changes until a final situation is reached.

The change of the viscosity of a Laponite suspensions without probe adsorbed on the surface indicate that the changes are not due to a redistribution of the adsorbed molecules. Apparently the structure of the colloidal clay suspension changes with time.

It is known that clay particles in rather concentrated suspensions aggregate. Indeed, a clay suspension is a lyophobic system and such systems are thermodynamically not stable. The system tends to minimalize the surface area in order to minimalize the interfacial Gibbs free energy, by means of an aggregation. Clay particles can undergo two kinds of aggregation : An edge-to-face and a face-to-face aggregation. The first kind occurs because the edges of clay particles are more or less positively charged, due to broken bonds of the crystal structure. These edges can therefore aggregate with the negatively charged faces. This results in a rather loose aggregation which can easily be destroyed by agitation of the clay suspension. The second kind of aggregation is due to the Van Der Waals attraction between the clay particles. This attraction is especially important between the faces of the particles, because these have the greatest dimension, and can eventually overcome the repulsion between the electrical double layers of the individual clay particles.

Probably, the time dependence of our experiments in diluted clay suspensions is due to such an aggregation of the clay particles. The diminution of the viscosity can be understood by assuming that after aggregation, the larger particles dissipate less energy during the flow than the individual particles. Another effect on the viscosity is also the decreasing number of particles after the aggregation. It is however difficult to quantitatively interpret these viscosity measurements because a clay suspension is certainly not an ideal system.

An increase of the particle size with time has also been observed by static light scatter measurements. Prior to such a measurement, the sample is made dust-free by pumping it through a millipore filter. When the sample is measured immediately, no angle dependence is observed. This means that the particle size is smaller than the limiting particle size. This limiting size amounts to 30 nm for our equipment. After several hours however, an angle dependence appears. This indicates a growth of the clay particles

An increase of the excimer formation efficiency after aggregation could be explained in two ways. If the molecules are only adsorbed at the external surface, aggregation increases the local concentration of the probe because the external surface decreases with aggregation. This assumption is however unlikely because the probe favours the aggregation. This means that the molecules are involved in the aggregation. Therefore it is more likely that after aggregation the adsorbed molecules are located between the clay particles. An analogue proposition was used by Turro et al. (7) to explain the increase of the emission decay time of $Ru(bpy)_3^{2+}$, adsorbed on Laponite, as a function of time. They stated that the decay time of $Ru(bpy)_3^{2+}$ adsorbed in the hydrophobic interlayers is larger compared to the one of the probes adsorbed at the external surface. In fact such a Laponite suspension, after aggregation, can be compared with a Hectorite suspension. Indeed, Hectorite always forms face-to-face aggregates. In the latter system excimer formation is also more efficient than for Laponite suspensions. It seems thus that excimer formation in face-to-face aggregates is more efficient than on the individual particles. A difference between a Laponite and a Hectorite suspension containing P3N is the excimer emission maximum. For Hectorite this maximum is situated at 475 nm. For Laponite, this maximum is situated at 480 nm and does not change with time. This indicates that both systems are not identical. Maybe, the individual clay platelets are not so strongly held together in the case of Laponite. An indication for this could be that aggregation for Hectorite occurs immediately while for Laponite it takes some time. The strongly attached platelets of Hectorite can indeed restrict the mobility of the adsorbed probes and therefore induce a more hypsochromic excimer emission.

The enhancement of the structural changes in the colloidal suspension after adsorption of the probe, as observed in the viscosity measurements, indicate that the aggregation is favoured. This can be explained by assuming a face-to-face aggregation. After adsorption the electrical double layer will become smaller and the Van Der Waals attraction higher, due to the hydrophobic molecules on the surface. The result of this will be a more efficient aggregation of the clay particles

The changes of the Laponite suspension is less pronounced when the sample is degassed every day. To degas the samples, Argon was bubbled through the suspension for several minutes. Probably, this agitation of the sample oppose the aggregation of the clay particles to some extent, resulting in a slower variation of the I_e/I_m with time.

D. SYNTHESIS OF A PYRENE LABELLED STERICALLY STABILIZED SILICA PARTICLE.

Introduction

Sterically stabilized silica particles can be prepared by coating the particle with an organic layer. Alcohols can be chemisorbed at the silica surface using the esterification method of Iler (8). This method is in fact a condensation reaction between the silanol groups (= the surface alcohol groups of the silica particle) and the alcohol. A long chain alcohol (octadecanol) was used to create the hydrophobic shell around the particle. By adding a small amount of 1-(1-pyrene)butanol to the reaction mixture we were able to label the particles.

synthesis and purification.

As a starting material we used a commercially available silica (Ludox HS 40, Dupont de Nemours). Ludox silica particles are made by exchanging the ions of sodium silicate solutions, ageing the particles formed and adding more silicate etc. (9). Using this procedure one obtains dense and homogeneous particles ($d = 2.2\ g.cm^{-1}$). The particle surface is covered with silanol groups. The silica is supplied as a dispersion in which the particles are electrostatically stabilized with sodium ions.

Reacting the Ludox particles with octadecanol requires the particles to be transferred from the aqueous solution to a melt of this alcohol. The aqueous dispersion was first deionized on a ion exchange resin (Merck) in order to improve the compatibility of the particles with the alcohol. 40 cm^3 deionized Ludox (i.e. 16 grams of silica) was added to 500 cm^3 1-propanol (P.A.-grade, Janssen Chimica) The water was removed by azeotropic destillation of the propanol-water mixture (79°). The silica in propanol dispersion was added to a melt of 75 grams octadecanol. Half a gram 1-(1-pyrene)-butanol was added to the mixture. The reaction mixture was refluxed at 180°C for two hours. During the reaction a dry nitrogen stream was led over the mixture (to prevent oxidation). The reaction was carried out in the dark.

The purification of the obtained hydrophobic silica particles involves mainly the removal of the unreacted alcohol. The reaction product is dissolved in chloroform, a very good solvent for the octadecanol. The particles are sedimented in a ultracentrifuge (35.000 rmp for 2 hours) the supernatans is discarted and the particles are solubilized in cyclohexane. Further purification is performed by repeated ultracentrifugation of the particles, discarting the supernatans and adding fresh cyclohexane. Evaporation of the solvent leaves a white powder that can be solubilized in different organic solvents.

Characterization and spectroscopy.

The particles can easily be dispersed in toluene. One obtains an almost completely transparant solution which points to a minor difference in refractive index between the particles and toluene. The quasi-elastic light scattering technique was used to determine the size of the particles in toluene. It revealed a diffusion coëfficiënt of $1.7\ 10^{-7}$ and a hydrodynamic radius of about 45.5 nm.

The absorption spectrum of the particles is shown in fig. 6. The emission spectrum is given in fig. 7. The emissionspectrum shows a typical pyrene fluoresence with a maximum at 377 nm and a very small excimer emissionband with a maximum at 480 nm. The excimer emission is probably due to the presence of multiple chromofores on the particle which are in close enough contact to form excimers upon excitation. Excimer formation between chromofores on different particles seemes unlikely. The dispersions become unstable at low temperatures. Even at temperatures as low as - 90°C no changes in the spectrum could be noticed. At these low temperatures the system is completely flocculated and one would expect a sharp rise in excimer emission if this emission was due to interparticle excimer formation.

Single photon timing measurments revealed that the excimers were formed dynamically. The rise time of about 15 ns in the excimer emission region was in good agreement with one of the components of the monomer decay (three-exponential).

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Fig. 1

RAMAN SPECTROSCOPY

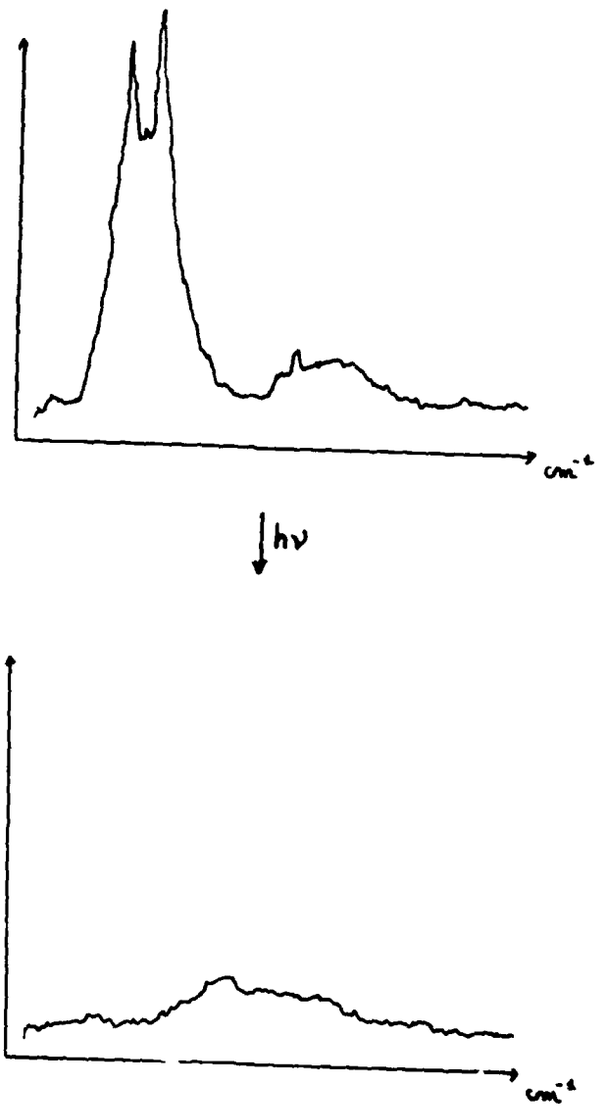


Fig. 2

POLYMERISATION ON A CLAY SURFACE

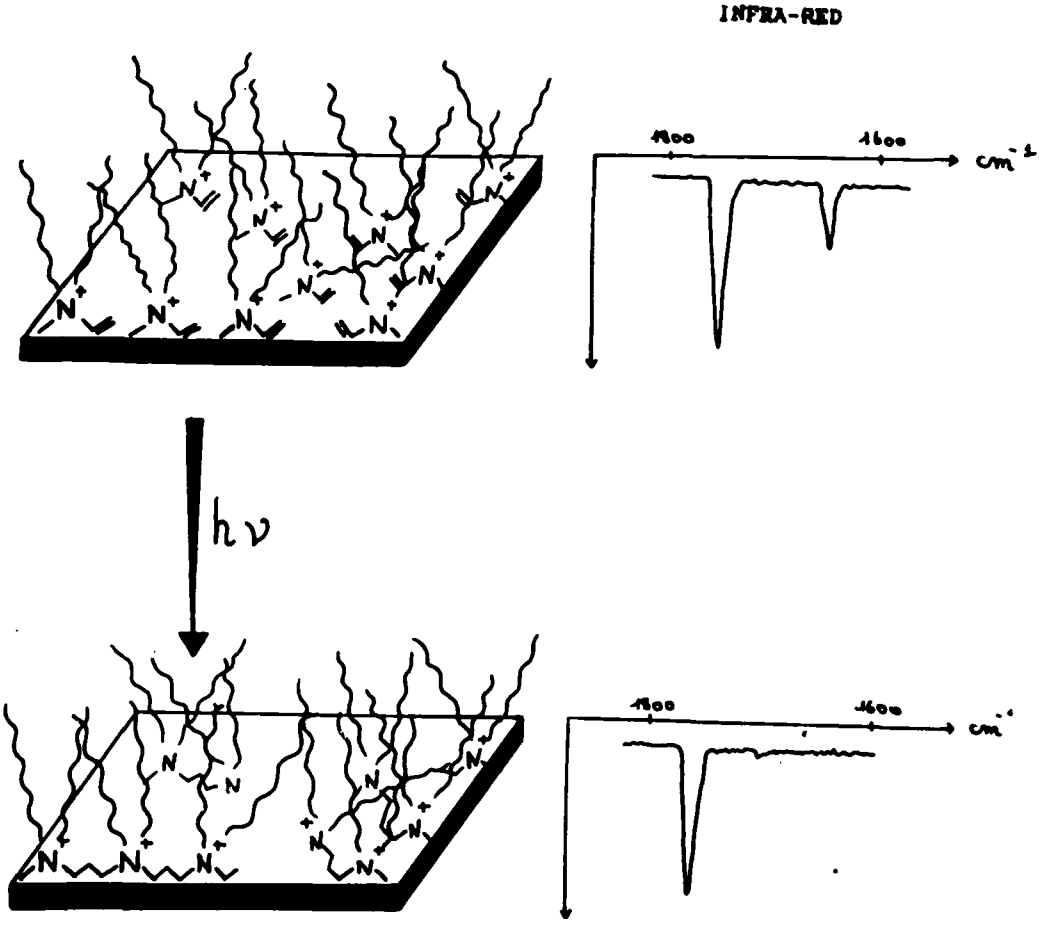


Fig. 3

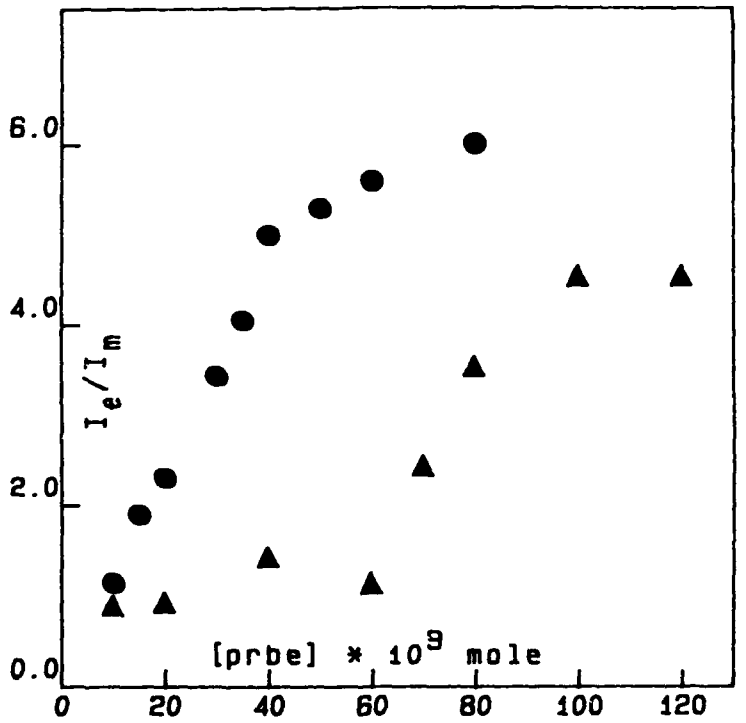


Fig. 4

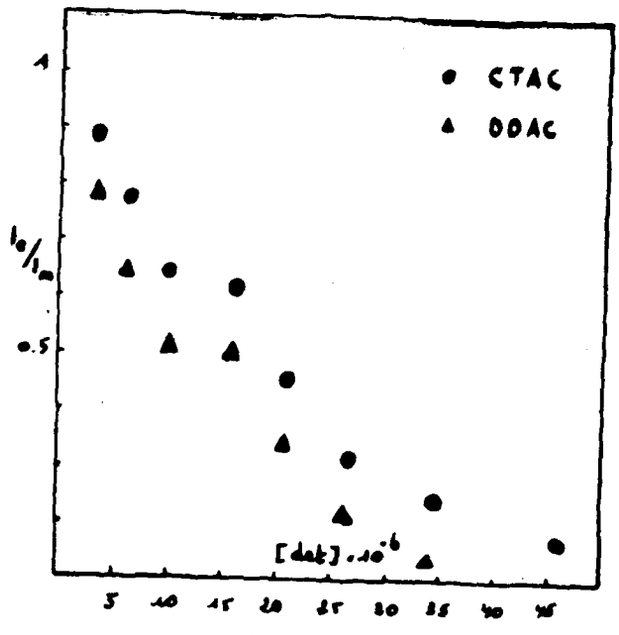


Fig. 5

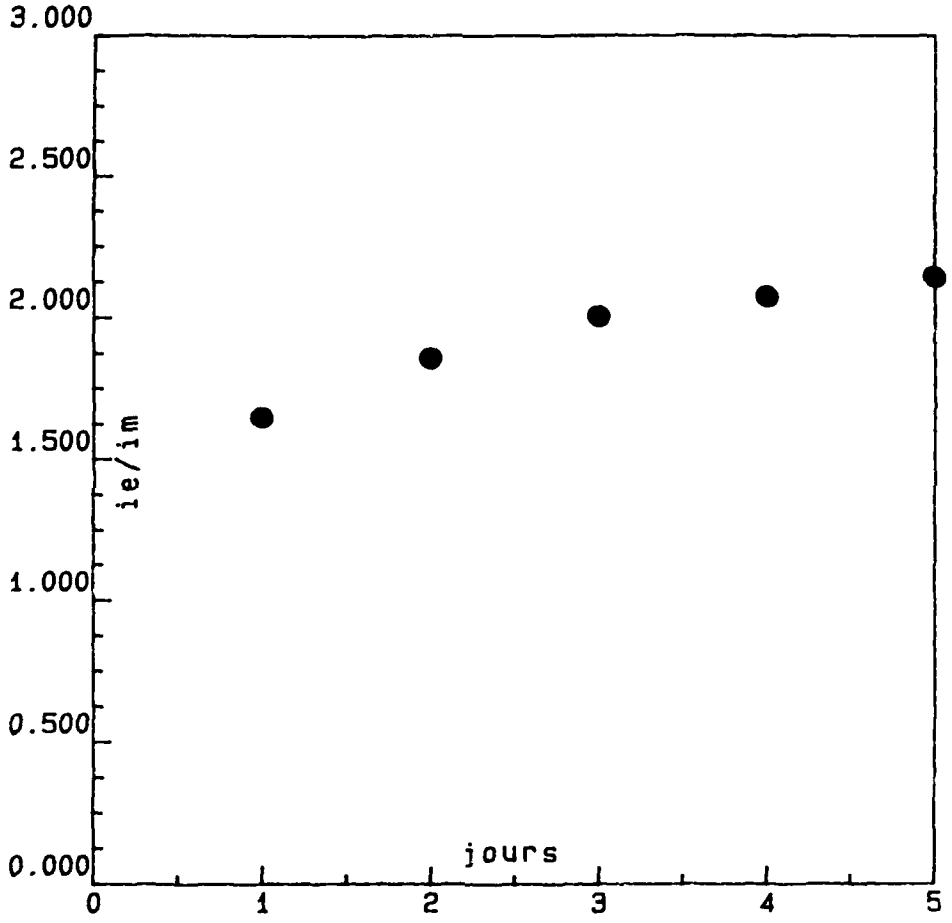
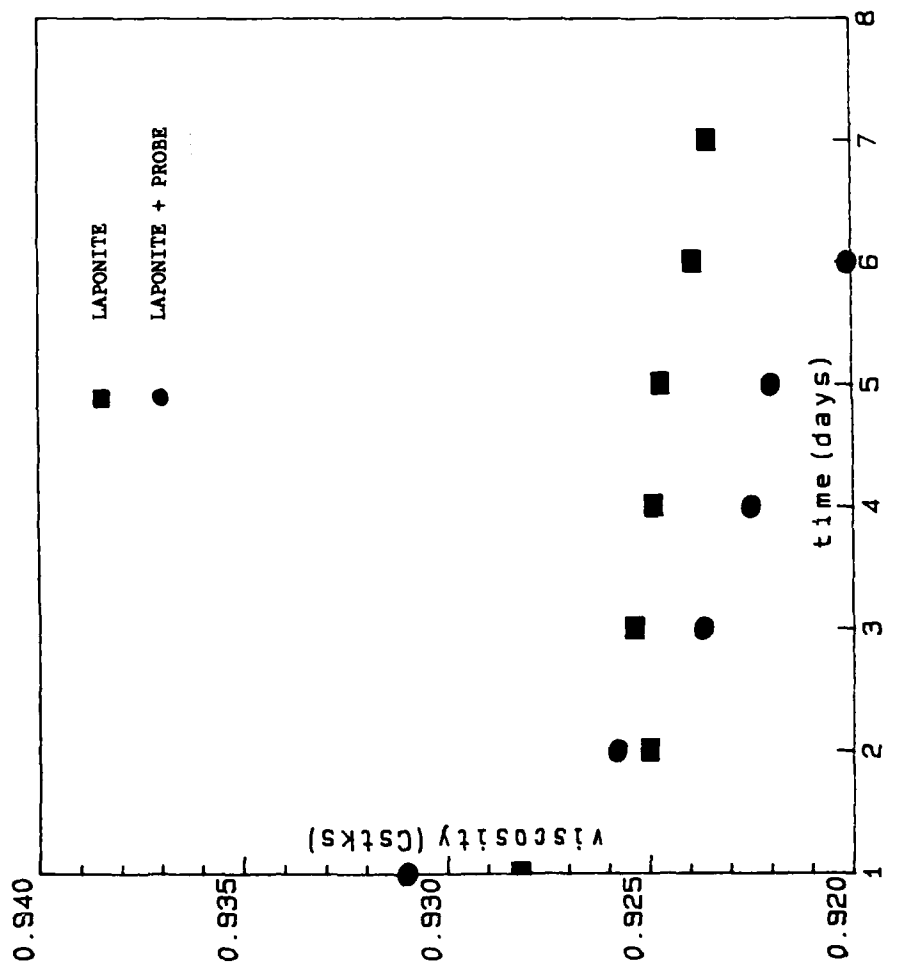


Fig. 6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LAPONITE + PROBE
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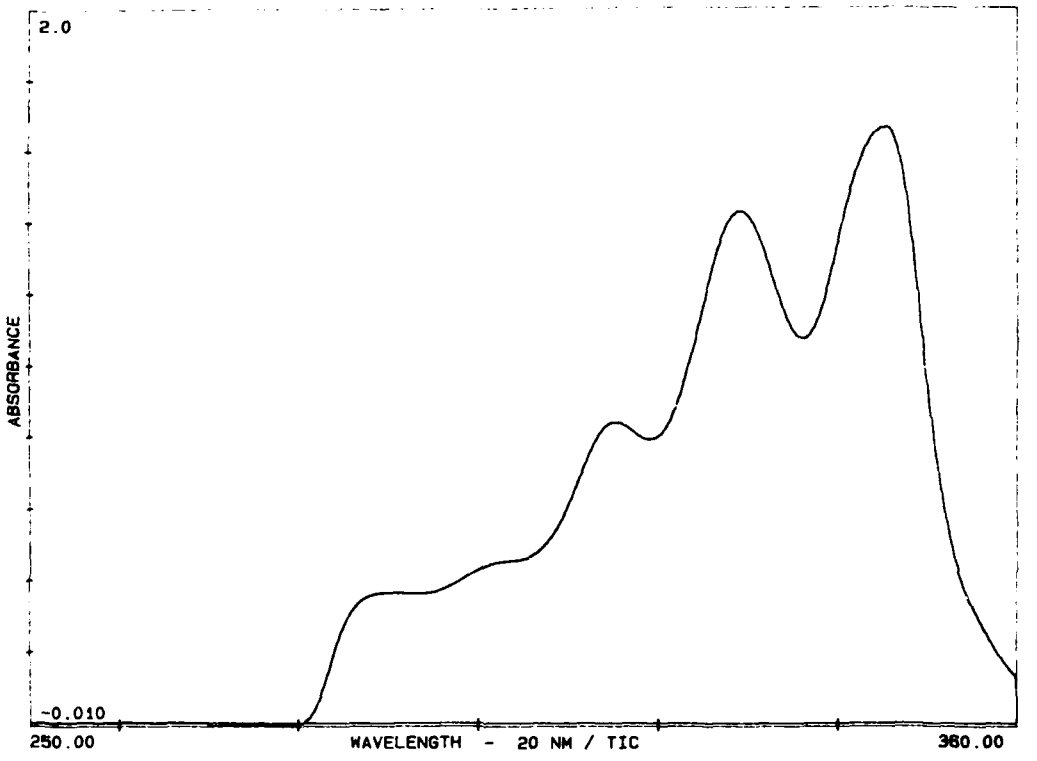
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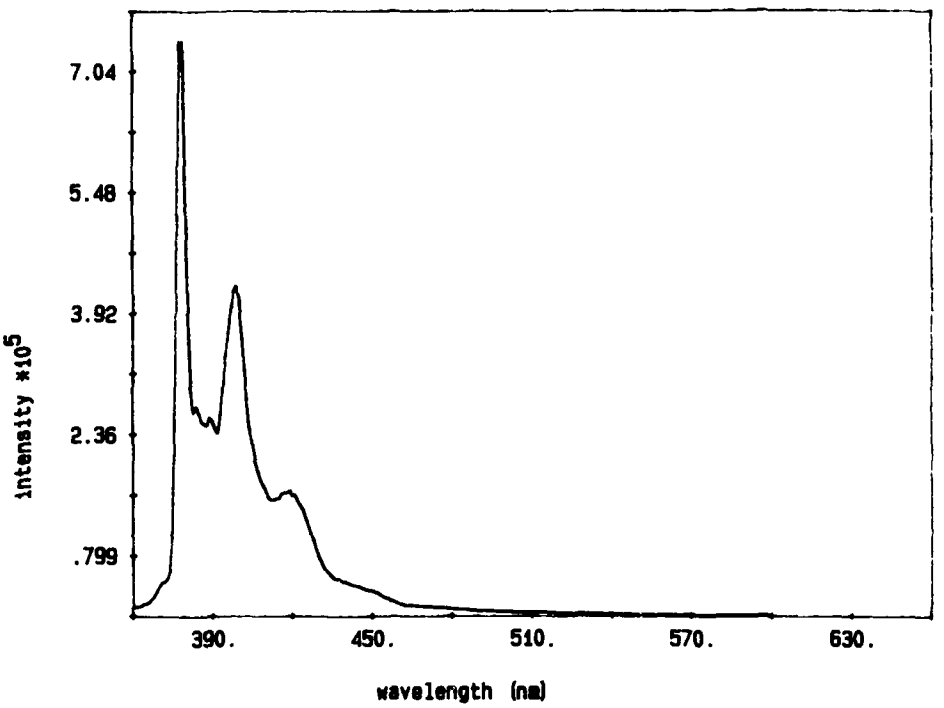
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